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A STUDY OF INTERNAL-FRICTION PEAKS IN TYPE 304 STAINLESS STEEL CONTAINING NITROGEN*

By Charles R. Manning, Jr., and John F. Eckel**

The occurrence of internal-friction peaks in body-centered cubic-type structures caused by interstitial atoms, such as nitrogen, has long been known. The mechanism to account for the internal-friction peaks in body-centered cubic-type structures has been described in detail by Snoek(1). A parallel-type study of internal friction in face-centered cubic-type structures has not progressed to a position where the present theories can account completely for the observed phenomena. The first study of interstitial additions to face-centered cubic-type structures utilizing internal-friction measurements was by Rozin and Finkel'shteyn(2) using 25 Ni - 20 Cr steel in 1953. Other work has been carried on since then by scientists of the Academia Sinica on pure nickel and manganese steels. This work, as well as the work in reference 2, utilized only carbon as the interstitial atoms, but results from both studies pointed to the fact that the peaks were induced by diffusion of the interstitial atoms in the face-centered cubic lattice. In the paper presented here, the effect of nitrogen additions on the internal-friction behavior of 18-8 face-centered cubic austenitic stainless steel was studied by the use of a torsional pendulum.

THEORETICAL

There have been two theories postulated to explain the internal-friction peaks found in face-centered cubic metals associated with interstitial atoms. Both theories are based on the formation and rotation of an atomic pair causing anisotropic lattice distortion and stress-induced diffusion.

The first theory was proposed by Cheng and Chang(3) and is explained in detail by Wu and Wang(4). The theory can best be explained using figure 1 where a vacancy is shown at the (1/2, 1/2, 0) position. It postulates that an interstitial nitrogen atom may jump into this vacancy, thus forming a substitutional nitrogen atom. This would cause a dissipation of a certain amount of thermal energy and if another nitrogen atom should jump into the previously vacated interstitial position, more energy would be released and a stable nitrogen pair would

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be formed. This pair would consist of an interstitial nitrogen atom and a substitutional nitrogen atom. The nitrogen pair is formed at (1/2, 1/2, 0) and A_1 positions and their axis is parallel to the A direction. Application of a compressive stress along the A-axis causes the interstitial nitrogen atom at position A_1 to jump to position B or a corresponding position in the C direction, thus providing some relief in the lattice strain. The nitrogen pair that was parallel to the A-axis or the load axis has rotated outward and is now normal to the A-axis. If a tensile load is applied along the A-axis through the nitrogen pair, a nitrogen atom that was in the B or C interstitial position will jump to the A_1 or A_2 position, corresponding to a rotation of the pair axis from a direction perpendicular to the tensile axis into a position parallel to it.

Cheng and Chang have stated that the stress relaxation resulting from the pair rotation induces the internal friction and that the mechanism for its generation is identical to that causing interstitial diffusion in α-iron. The only difference is the distance traveled by the atoms. In a body-centered cubic lattice, the interstitial atom moves $1/2\ a_o$ per jump along the $\langle 010 \rangle$, while in a face-centered cubic lattice, the movement is $\frac{\sqrt{2}a_o}{2}$ along $\langle 110 \rangle$ (where a_o is the lattice parameter).

They also postulated that because of the similarity of the diffusion peaks, the formula governing the peak magnitude for body-centered cubic lattices is applicable and that the effect of interstitial concentration on E_m (the unrelaxed modulus of elasticity) and E/N_r (the change in strain per unit volume caused by rotation of the axis to a direction parallel to the tensile axis) can be neglected in the face-centered cubic lattice giving

$$Q_{max}^{-1} = \frac{CN_F}{T_1} \qquad (1)$$

where Q^{-1} is the peak height, T_1 is the peak temperature, N_F is the concentration of interstitial pairs and C is a constant. Nitrogen pairs are formed by interaction between nitrogen atoms that have jumped into vacancies and their interstitial nitrogen neighbors. The number of pairs N_F under a fixed nitrogen concentration can be determined by: (1) the concentration of vacancies and by (2) the state of the nitrogen distribution. Each of these is sensitive to temperature fluctuations and can be determined as follows. The number of vacancies frozen in the crystal depends upon the cooling rate of the specimen.

(1) Wu and Wang[4] have investigated the number of lattice vacancies available in a face-centered cubic lattice. Their investigations with ferrous alloys were made by quenching wire specimens from 1200° C to below 350° C where the vacancies were assumed to be immobile. The cooling rate was estimated from the following equation:

$$\frac{\partial T}{\partial t} = \gamma\left(\frac{\partial^2 T}{\partial t^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) \qquad (2)$$

where γ is thermal diffusivity and r is the radius of the wire. Their calculations indicated that a cooling time from 1200° C to 350° C of 0.04 second was achieved. The majority of the supersaturated vacancies did not have a chance to move and were frozen in. Thus, at the temperature of most internal-friction measurements, the lifetime of the vacancies is probably that of several years.

(2) The state of the nitrogen atoms or redistribution is a function of the activation energy E_F for vacancy formation. A specimen with constant vacancy concentration, such as being delt with in internal-friction studies, should have an increasing nitrogen pair concentration with decreasing temperature if the atoms have enough mobility to attain thermal equilibrium at each temperature.

Their theory also states that the height of the internal-friction peaks varies parabolically with low nitrogen concentration and linearly with high nitrogen concentration.

The second theory put forward to explain internal-friction peaks in face-centered cubic lattices was recently published by Tsien[5]. A second face-centered cube shown in figure 2 is used to describe their theory. The interstitial positions A and B are occupied by an atomic pair. The very presence of the interstitial pair can cause an anisotropic distortion in the lattice. In the A - B direction, the distortion of the cube is greater than in a direction normal to it. Applying a tensile stress in the Z direction will cause either atom A or atom B to become unstable and one will be forced to jump to either position C, D, E, or F to relieve the lattice strain. This will position the pair so that the angle between them and the direction of the stress is a minimum. This causes a maximum relaxation to be obtained, whence arises more anelastic deformation in the direction of the stress. It is the same nature as internal-friction peaks in body-centered cubic lattices caused by interstitial atoms. Tsien states that the activation energy of the internal-friction peaks is equivalent to the activation energy of the diffusion of interstitial atoms and the peak height is proportional to the number of nitrogen pairs. Statistical theory indicated that the number of interstitial pairs is proportional to the square of the interstitial content.

EXPERIMENTAL PROCEDURE

The apparatus used to conduct the internal-friction tests consisted of a torsional pendulum which was fashioned after the equipment designed by Ke[6]. The frequency of vibration covered a range of 0.33 to 1.1 cycles per second.

All specimens were in the form of 0.025-inch-diameter AISI 304 austenitic stainless-steel wire that had been cold drawn. The heat analysis of the wire is given in table I and a nitrogen analysis by Allegheny-Ludlum Steel Corporation showed 0.05-percent nitrogen. Andrews[7] stated that cold drawing causes some of the austenite to be transformed to α-iron. To make sure that the wire used in this investigation was fully austenitic, specimens were encapsulated in an evacuated Vycor tube and solution heattreated 48 hours at 1025° C and water quenched. Another set of wires from the same coil was nitrided by placing them in a furnace for 40 hours at 925° C and passing ammonia through the furnace. The ammonia dissociated and entered the lattice as monatomic nitrogen. The nitrogen was found to be driven well into the lattice of the wire as shown in figure 3 by the heavily nitrided case. These wires were then encapsulated and heattreated as stated before. The solution treatment was designed to drive nitrogen through the lattice and produce a homogeneous structure. All wires subjected to the solution treatment were placed in small ceramic tubes within the evacuated Vycor glass tube. This served as an effective method to remove camber and to provide straight specimens.

RESULTS AND DISCUSSION

The study was originally initiated to determine whether interstitial nitrogen could cause internal-friction peaks in austenitic stainless steel. If it did induce relaxation peaks in the austenite, it was also the purpose to determine both activation energy and the diffusion constants for nitrogen diffusion in austenite. The frequency of vibration was varied during the investigation to allow activation energy calculations from maximum peak shifts.

Figure 4 shows the relaxation spectrum for the unnitrided 304 stainless-steel wire which was solution heattreated 48 hours at 1025° C and water quenched to maintain the austenitic structure. It was then tested at 1.05 cycles per second. No major peaks were recorded below 325° C and the peak starting at 325° C is believed to be a grain boundary relaxation peak. A very small peak at 160° C is believed to be associated with stress-induced formation of ferrite or quasi-martensite because the wires became slightly magnetic after testing. A metallographic examination before and after testing revealed no major structural changes and did not show ferrite.

The relaxation spectra for heavily nitrided and solution heattreated specimens are shown in figures 5 to 7. The frequency of vibration employed in figure 5 was 1.09 cycles per second. A major peak was noted in the spectrum with a maximum amplitude at 210° C which is believed to be caused by nitrogen. This peak was noticeably absent in the spectra of the unnitrided wires. The spectrum shown in figure 6 is for a vibrational frequency of 0.57 cycle per second and a major peak was noted with a maximum at 200° C. The upper spectrum in figure 7 was obtained with a frequency of 0.33 cycle per second and the major peak shifted to a still lower temperature of 192° C. After making this run, it was decided to cool the same specimen without removal from the apparatus and make an additional run. This resulted in a new relaxation peak at a much higher temperature, 249° C, but with a much lower amplitude. The results of this run are shown in figure 7.

Ke and Yang[8] have reported that the separation and precipitation of carbon or other interstitial atoms, such as nitrogen, from solid solution, not only has the effect of lowering the amplitude of the internal-friction peaks, but also shifts the peak towards a higher temperature as experienced here. It was felt that the nitriding and solution heat treatment drove an excessive amount of nitrogen into the interstitial positions of the lattice.

Thus, supersaturation is indicated prior to the first run in figure 7. Evidence to support this was found by X-ray diffraction measurements. The normal iron-face-centered cubic lattice parameter as reported by Dykstra[9] is 3.54 Å. The atomic radius of Fe is 1.26 Å. The 304 austenitic stainless steel contains 18-percent chromium and 8-percent nickel in solid solution as the major alloying elements. The atomic radii of these two are only 1.28 Å and 1.25 Å, respectively. Therefore, not much increase in the lattice parameter would be expected and Ke and Wang[10] reported a value of 3.62 Å. A Debye Sherrer pattern of the nitrided wire was made and the lattice parameter was found to be 4.15 Å. This indicated that the lattice was considerably expanded by nitrogen. Ke and Yang[8] have stated that the amplitude of the relaxation peak is a function of the amount of the interstitial atom in solution. A nitrogen analysis showed 2.20-percent nitrogen in the alloy after nitriding and solution heattreating. The decrease in amplitude is interpreted as resulting from formation of additional nitrides and lowering of the amount of nitrogen in solid solution. The microstructure before and after testing indicated many more nitrides were formed as the result of testing. A third run was made on the same specimen which produced an almost identical relaxation spectrum with that of the second. The magnitudes of the internal-friction peaks were essentially equal, indicating the amount of free nitrogen in the interstitial positions of the lattice had been stabilized. A fourth run was made at a higher frequency (0.66 cycle per second) to displace the peak and permit calculation of the activation energy from these peaks. The peak temperature was 264° C and the amplitude of the peak is comparable to the amplitude of carbon peaks found by Ke and Wang[10] in 18-8 stainless steel.

The use of various vibrational frequencies produced relaxation peaks at various temperatures which provided sufficient data to calculate the diffusion coefficient of nitrogen in austenite. These calculations were based on the assumption that the peaks being utilized were associated with a single relaxation time and that the process is diffusion controlled. The activation energy was obtained by calculation from data shown in figures 5 to 7 using the following equation:

$$\Delta H = 2.3R\left(\frac{\log f_1}{1/T_2} - \frac{\log f_2}{1/T_1}\right) \qquad (3)$$

where f is the vibrational frequency in cycles per second and T is the absolute temperature. It was found to be 28,700 calories per mole for the supersaturated solid solution and 25,800 calories per mole for the saturated solid

solution. Values of activation energy for diffusion of carbon in α-iron reported by Wert[11] and in austenitic 18-8 stainless steel reported by Ke and Yang[8] were 20,000 and 30,000 calories per mole, respectively. Thus, the calculated values of 25,800 to 28,700 calories per mole found for the activation energy of nitrogen diffusion in austenite seem to be very reasonable.

There appear to be some limitations to calculation of activation energy for the nitrogen diffusion in austenite by the above method. Calculation of the activation energy for nitrogen diffusion in austenite from half width measurements as suggested by Stephenson[12] gives values of 8,500 calories per mole which is much less than the expected value of 17,500 to 19,500 calories per mole. This is approximately 2/3 of the 25,800 to 28,700 calories per mole found by the frequency change measurements. The 2/3 value would be expected from measurements on body-centered cubic lattices. Cheng and Chang's theory considered interstitial atoms jumping into vacancies. If this were so, it would seem that the activation energy for stress-induced microdiffusion should be much lower than the activation energy found for macrodiffusion. Ke, Tsien, and Misek[13] found that the microdiffusion measurements for carbon atoms were slightly higher than the macrodiffusion measurements made by radioactive C^{14}. The theory of Tsien which does not depend on lattice vacancies and interstitial atoms jumping into substitutional positions would predict that the activation energy for microdiffusion would be equal to that of the macrodiffusion and experimental discrepancies could give slightly higher values for either. Therefore, the theory of Tsien appears to be more plausible.

Ke and Yang[8] showed that internal friction induced by carbon in austenitic stainless steels with a manganese content of 1.7 percent was similar to pure nickel and from this it was concluded that the internal-friction peak was caused by rotation of interstitial atomic pairs. For alloys containing large amounts of alloying elements, the situation appears quite different and these alloying elements may influence the interstitial atoms to a large degree. If one of the alloying elements shows a greater affinity for interstitial atoms than another, it may reduce the opportunity for the formation of the interstitial atomic pairs and may instead cause the formation of an alloying element interstitial pair. This would induce a number of relaxation times and complicate the interpretation.

Laxar, Frame, and Blickwede[14] have shown that a relaxation peak might be interpreted to have a single relaxation time, but in reality may have multiple relaxation times. The activation energy can be calculated for a shift of any point on the relaxation peak as noted by Wert and Zener[15]. This type analysis was applied to the curves in figures 5 to 7 for both the upper and lower side of the curve from 10 to 60 percent of peak height on the lower temperature side and from 10 to 70 percent of the peak height on the high temperature side. The results are plotted in figures 8 and 9 and an average activation energy was calculated for each set of data. The value for the lower side activation energy was 22,000 calories per mole and for the upper side 32,000 calories per mole. The semi-log plots of frequency versus reciprocal of the absolute temperature, show the experimental points are connected by lines with activation energy values of 22,000 and 32,000 calories per mole. The results show very little scatter,

although the results on the low-temperature side are not as consistent as on the high-temperature side. This consistency is a good indication that there are probably two separate relaxation times involved in this peak and in figure 10, the dotted line gives the probable breakdown of the involved peaks.

The question remains, what is causing the two relaxation peaks found in the austenite. One peak is probably caused by the rotation of the interstitial nitrogen pairs and the other must be caused by an interaction between the nitrogen and an alloying element. It has been reported that when manganese is added to iron-carbon alloys, it may reduce the opportunity for formation of interstitial atom pairs. Thus, there may be a greater probability of formation of manganese-carbon atom pairs. In steels with a high manganese content, the internal-friction peak is caused by manganese-carbon atom pairs and not by carbon-carbon atom pairs. The amount of manganese in this alloy is not expected to interact in this way with the nitrogen nor is Si, although silicon nitrides have been identified. The second peak is probably caused by an interaction with chromium. A nitrogen-chromium interaction has been reported by Dijkstra and Sladek[16]. No evidence of nickel interaction with the nitrogen could be found in the literature. More work on face-centered cubic materials is needed to help identify the mechanism responsible for the broad relaxation peaks. It is believed that the first peak with an activation energy of 22,000 calories per mole represents nitrogen pair activity and that the second peak with an activation energy of 32,000 calories per mole is associated with the interaction between nitrogen and chromium. It is also felt strain aging may account for some of the internal friction.

CONCLUSIONS

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The addition of nitrogen to 18-8 type austenitic stainless steels caused relaxation peaks to appear on the internal-friction spectra. These peaks appear to be much broader than nitrogen-induced peaks in body-centered cubic structures and there is a strong indication that the peaks are not the results of a single activation process. A detailed analysis indicates the major peaks probably contained two smaller peaks with activation energies of 22,000 and 32,000 calories per mole. The lower temperature peak was probably caused by the rotation of the interstitial nitrogen pairs while the other one was probably caused by the interaction of the atomic nitrogen with chromium as a major alloying element. The amplitude of the peak also appears to be a function of the amount of nitrogen in solid solution.

Author

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TABLE I

HEAT ANALYSIS OF TYPE 304 STAINLESS-STEEL WIRE

C, percent	0.070
Mn, percent	1.02
P, percent	0.020
S, percent	0.026
Si, percent	0.51
Cr, percent	18.46
Ni, percent	10.28

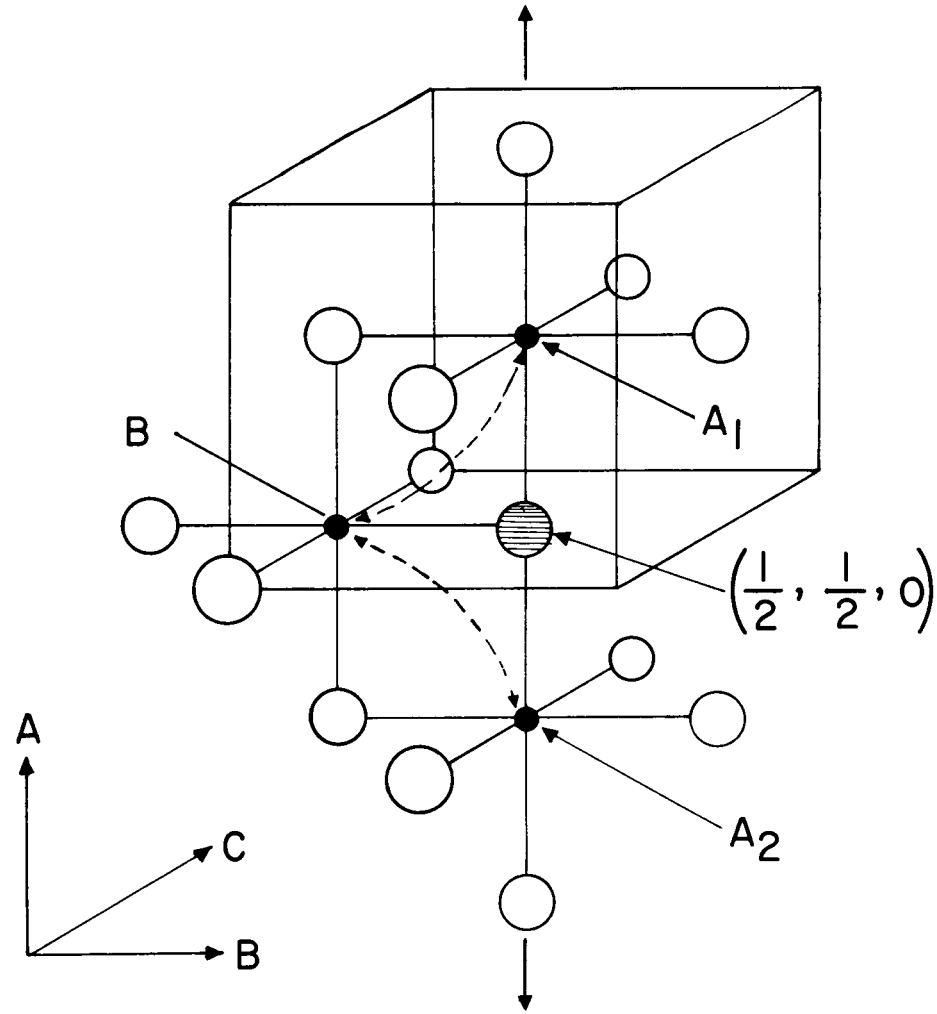

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Figure 1.- Interstitial atom pair diffusion in cubic lattices according to Cheng and Chang[3].

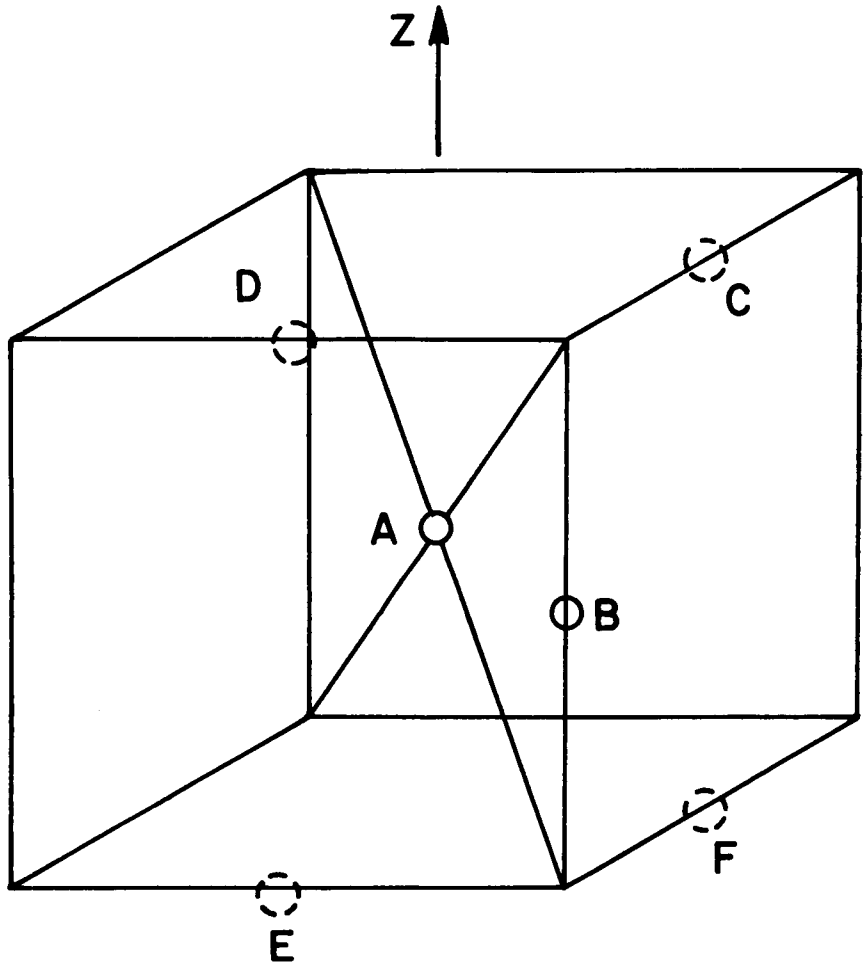

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Figure 2.- Interstitial atom pair diffusion in cubic lattices according to Tsien[5].

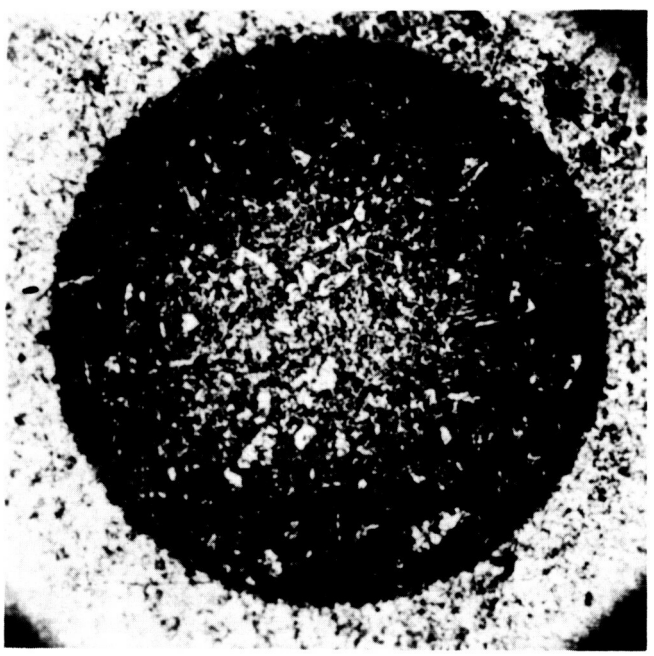

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Figure 3.- Nitrided case on type 304 stainless steel.

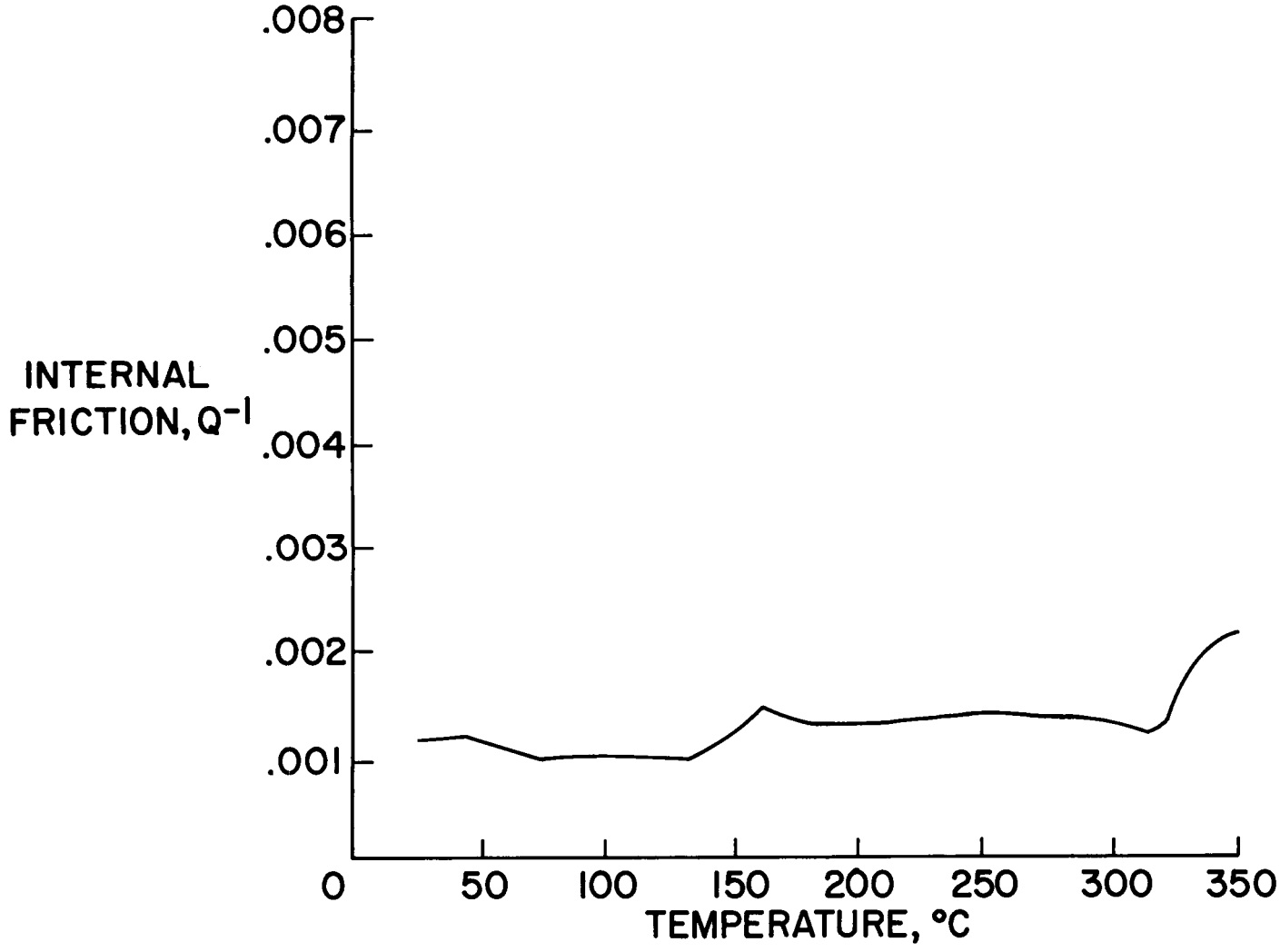

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Figure 4.- Relaxation spectrum at a frequency of 1.05 cps for unnitrided type 304.

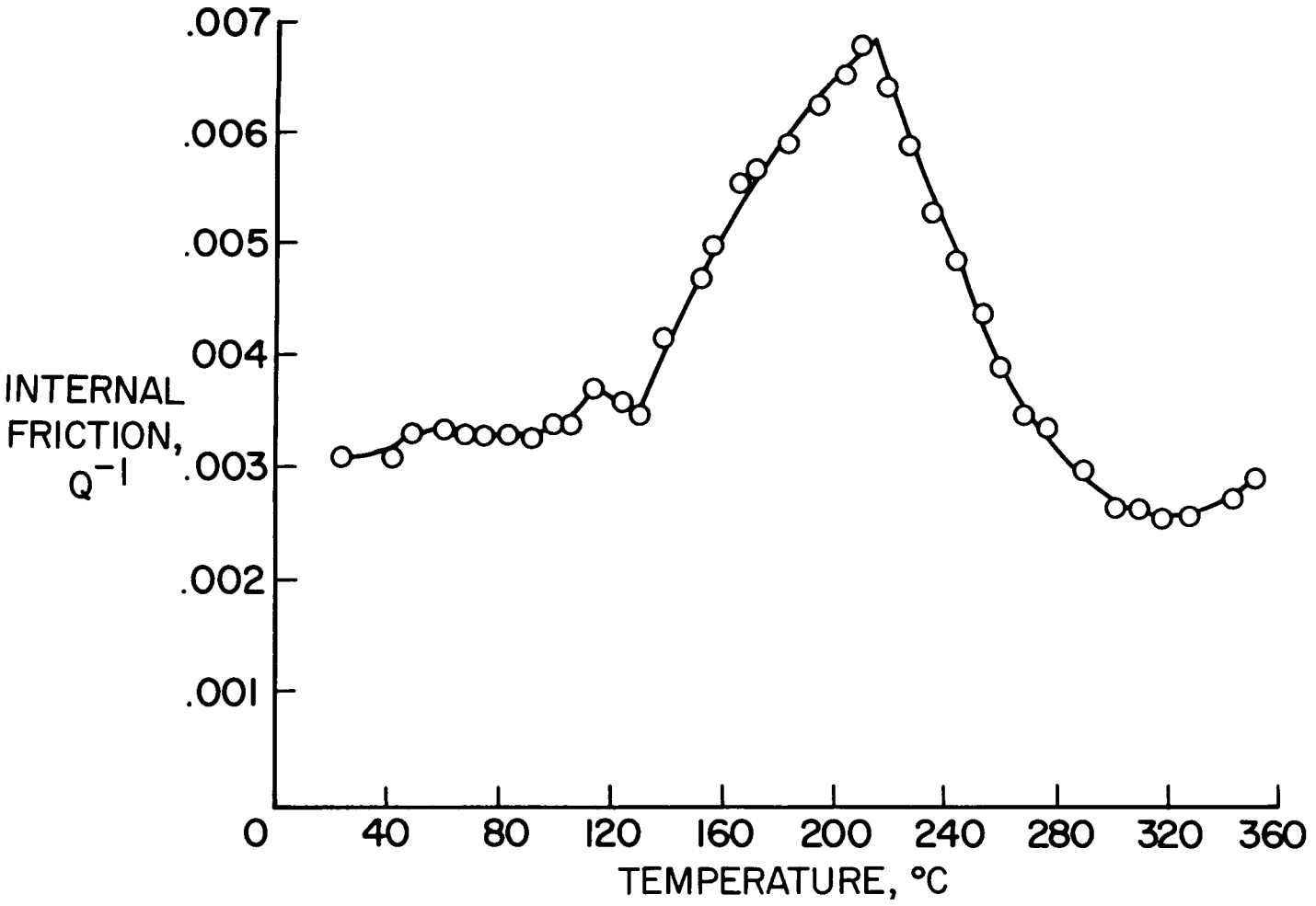

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Figure 5.- Relaxation spectrum at a frequency of 1.09 cps.

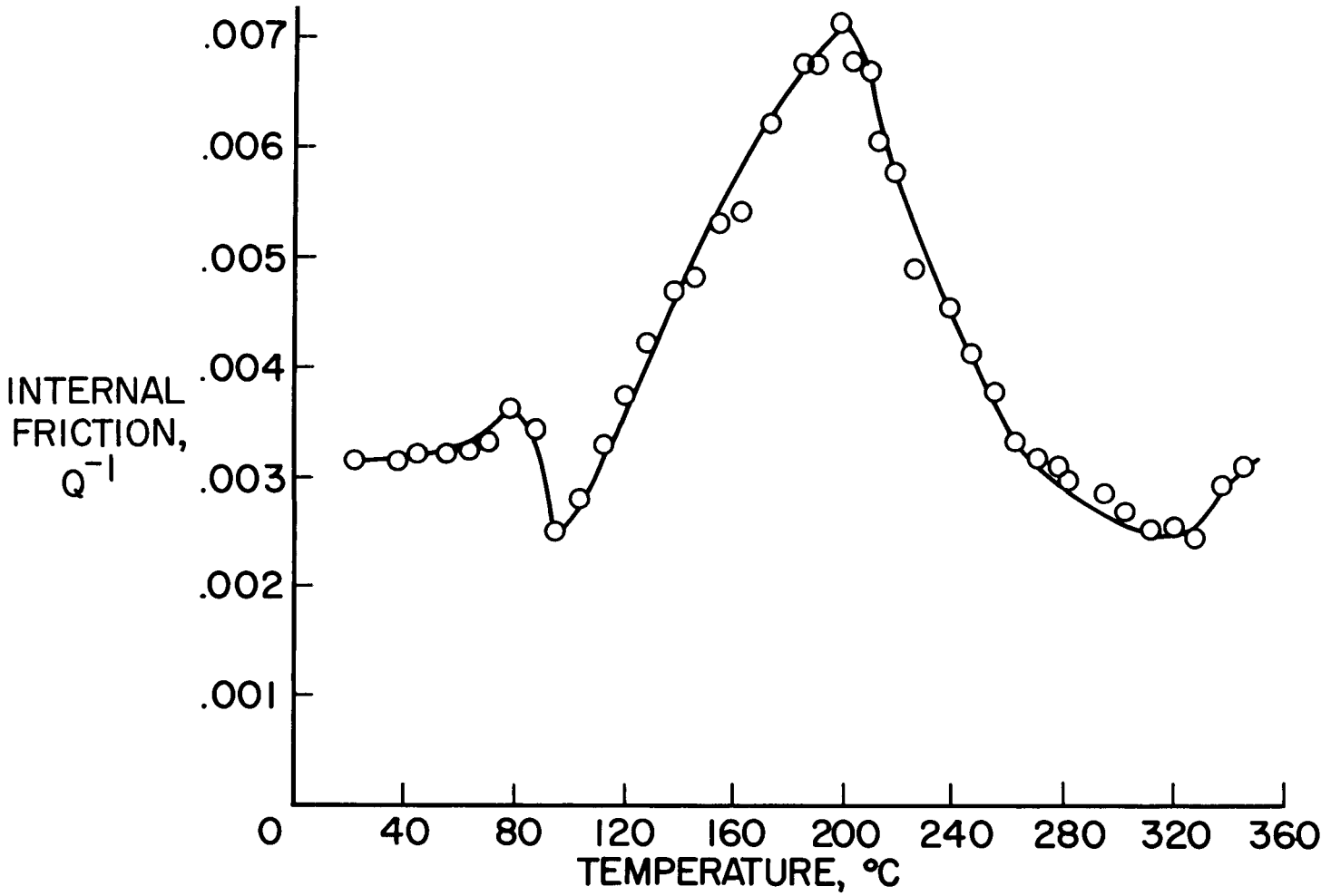

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Figure 6.- Relaxation spectrum at a frequency of 0.57 cps containing nitrogen.

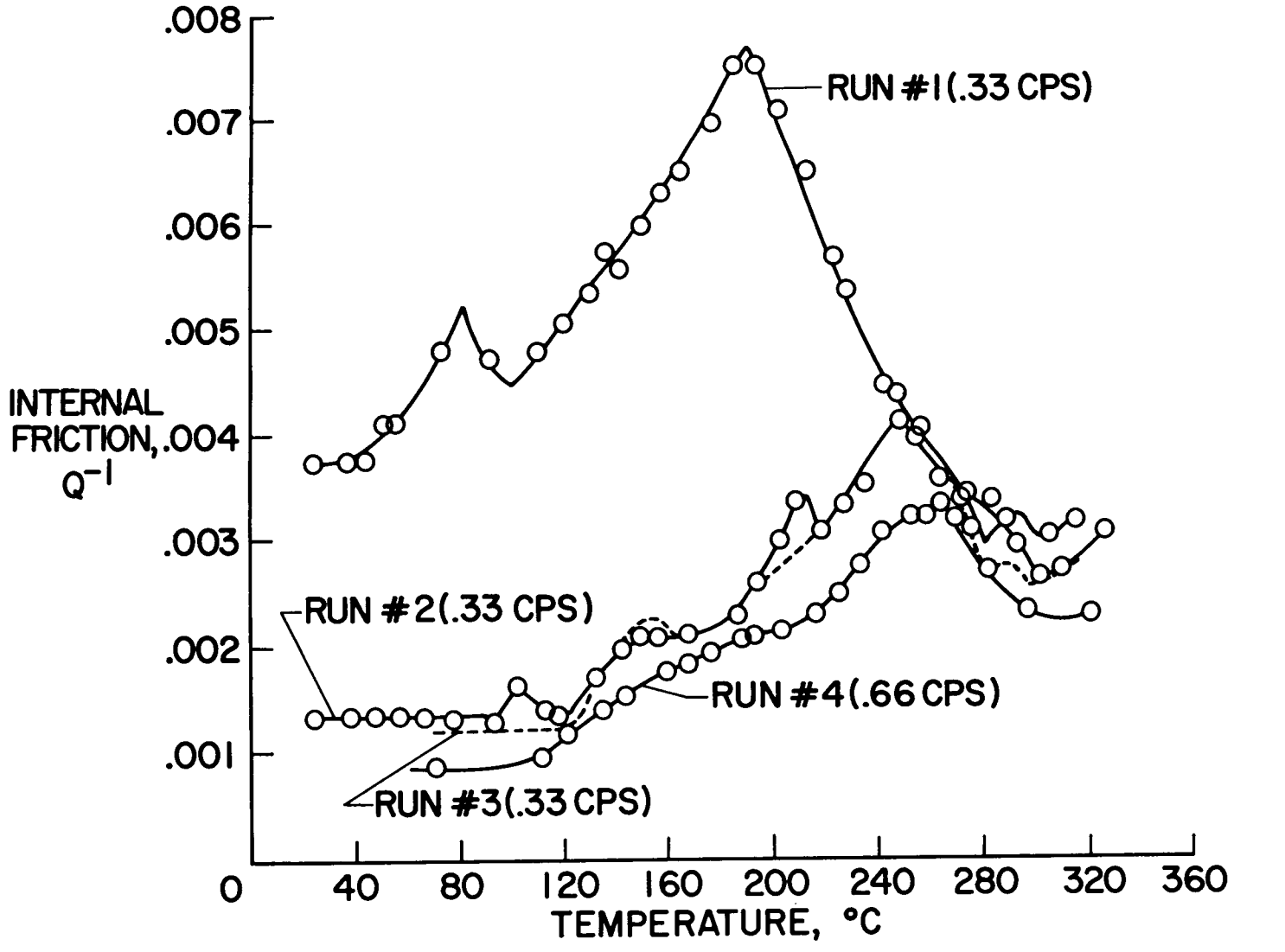

Figure 7.- Relaxation spectra for type 304 containing nitrogen.

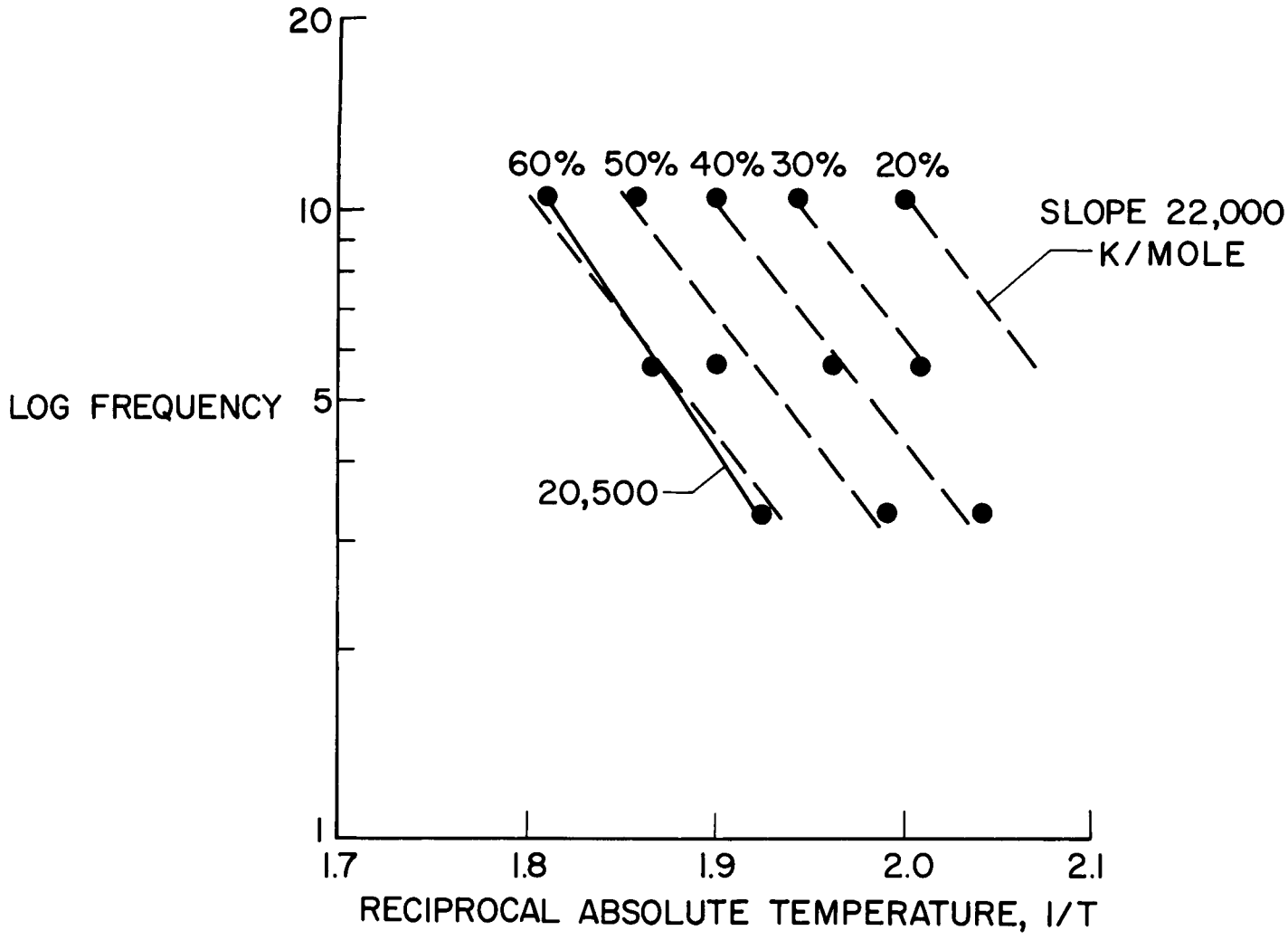

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Figure 8.- Relationship between frequency and absolute temperature on lower side of peak.

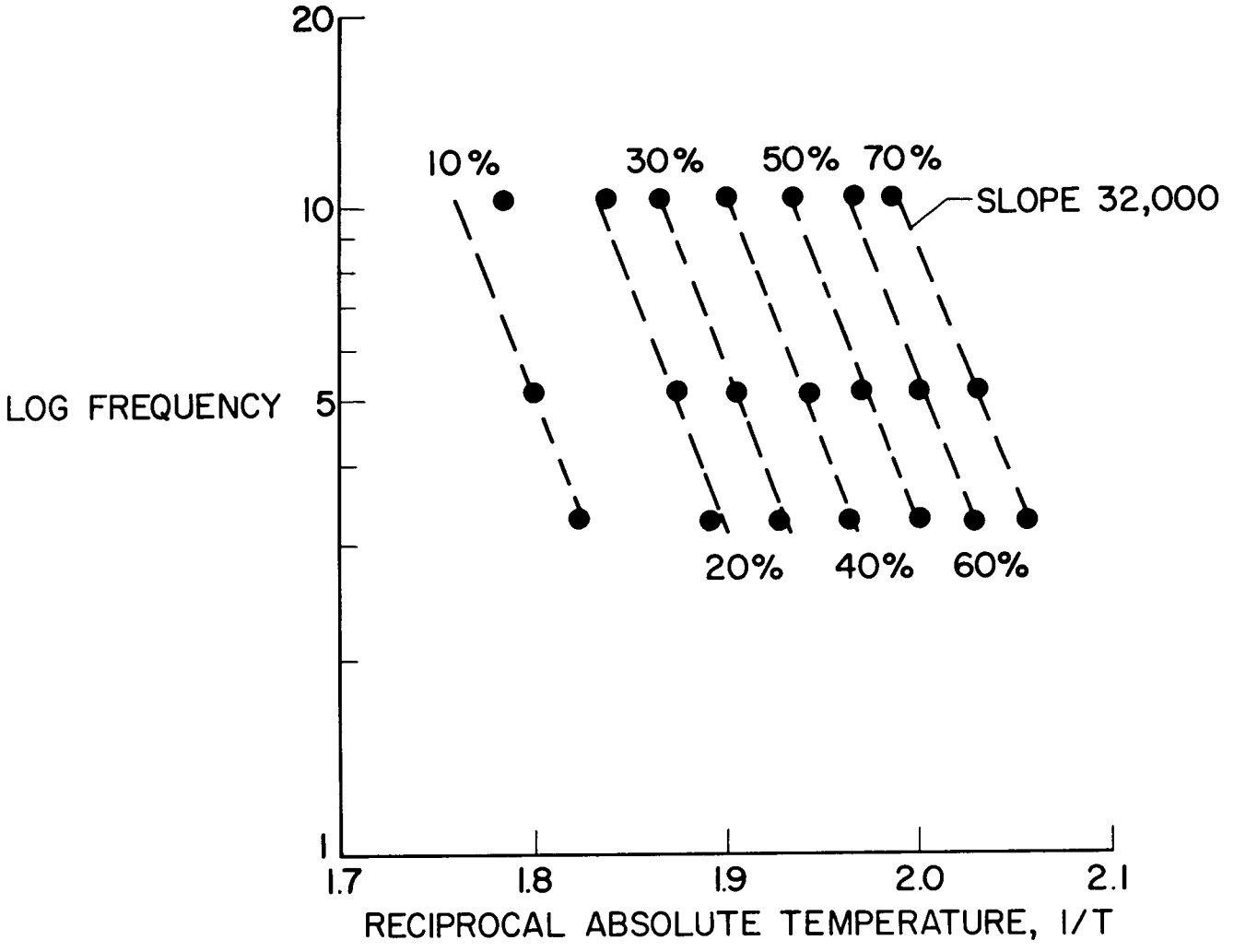

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Figure 9.- Relationship between frequency and absolute temperature on upper side of peak.

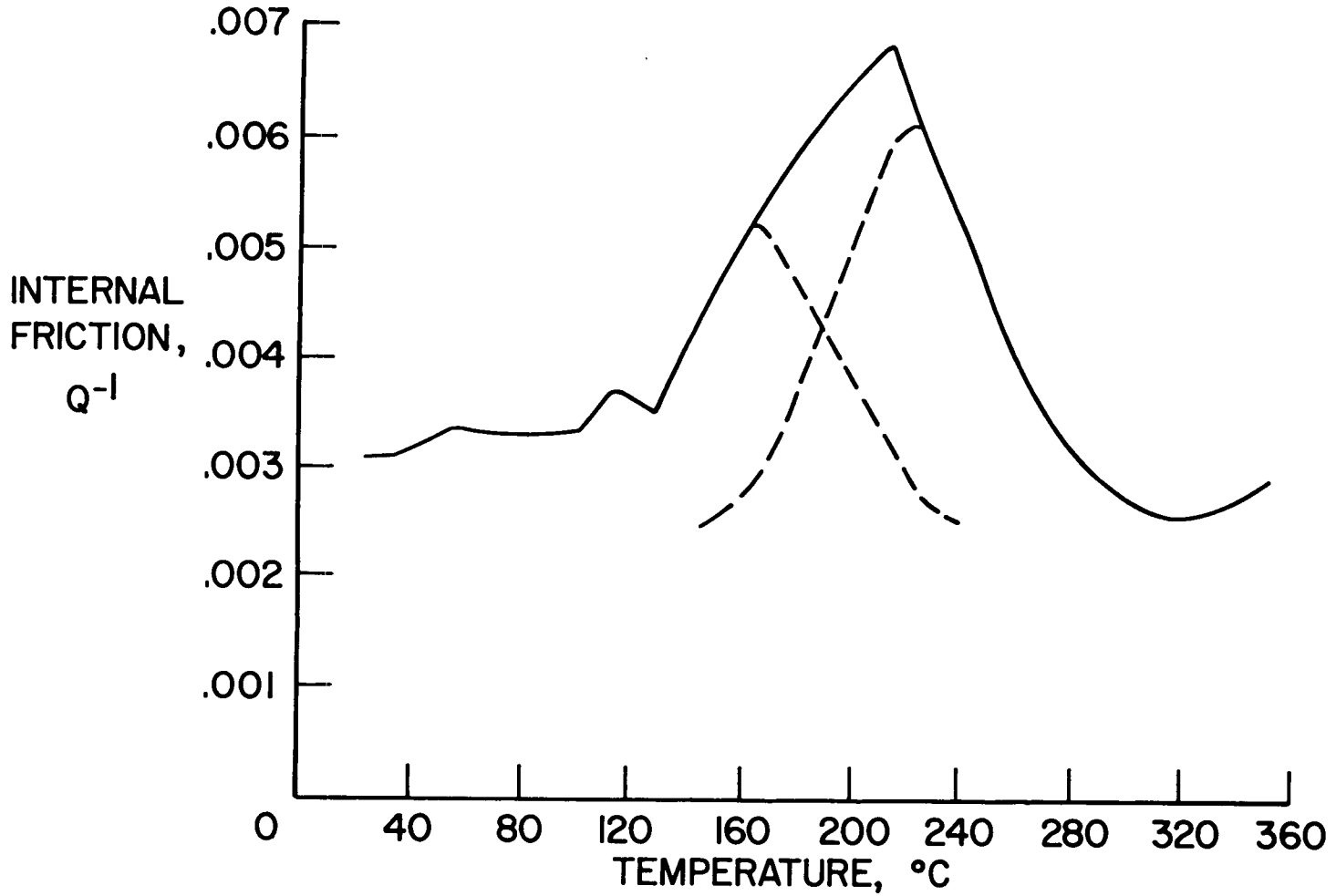

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Figure 10.- Probable form of double peak in the relaxation spectrum.